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Chemical Physics Letters 568–569 (2013) 75–79

Contents lists available at SciVerse ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Molecular interactions between fullerene C_{60} and ionic liquids

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ARTICLE INFO

Article history:
Received 22 November 2012
In final form 4 March 2013
Available online 15 March 2013

ABSTRACT

Structural and energetic aspects of solvation of fullerene C_{60} in ionic liquids at room temperature were analyzed by using atomistic molecular dynamics simulations. Ethylammonium Nitrate (EAN) and 1-Butyl-3-Methylimidazolium Tetrafluoroborate (BMIMBF4) ionic liquids were conveniently chosen for presenting different polarities. Analysis of the spatial distribution of the ionic liquid revealed different patterns for the solvation of C_{60}. Energetics indicated that the presence of C_{60} weakened the ionic interactions in solution compared to those in pure liquids. Our free energy calculations showed that there is an energy cost of 235 kJ mol^{-1} for transferring fullerene C_{60} from BMIMBF4 to EAN.

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1. Introduction

Ionic liquids are a class of organic salts with unusual low melting temperature that are gaining considerable attention due to their enormous potential for industrial applications [1–5]. Their ionic components can be adjusted by different functional groups or ionic combinations to improve the degree of structuring in the liquid phase, distinguishing the ionic liquids from the conventional solvents and solutions containing molecular ions dissociated [5]. The ionic liquids present a set of remarkable properties [2–6] such as, high viscosity, non-flammability, thermal stability, electrical conductivity and good solvation properties for both polar and nonpolar solutes, that make them a clean alternative to the current organic solvents [2,6].

In ionic liquids, the balance of intermolecular forces is complex and the modulation of their properties depends essentially on the choice of anions and cations that constitutes the liquid [7,8]. Cations are formed by a polar group, where most of its electrostatic charge is localized, and an aliphatic apolar group, whereas anions are generally symmetrical and nonpolar [7–9]. These cations and anions form a polar network due to their strong electrostatic interaction, whereas the nonpolar groups form domains assembled? by van der Waals short range interactions [1,7,10]. The formation of polar and nonpolar domains in ionic liquid has established a new way of analyzing the solvation process [1,7,10,11]. Depending on the polarity of the solute it can lie in one domain or in another. Also, depending on the polarity of the ions (in particular, of the cations) the ionic liquid may be more or less polar, which also affects the solvation of a given compound. For example, studies on the solvation of methane and ethane showed that the solubility increases with the size of the alkane chain, which cannot be explained by the free volume or electrostatic solute–solvent interactions [1,12]. In these cases the solubility of methane and ethane is probably determined by the size of domains in ionic liquid [7,10]. In short, the solvation in ionic liquids can occur through several different solute–solvent interactions, including ionic interactions, dipole interactions, hydrogen bonds, van der Waals forces and aromatic interactions [7,10,13–16].

Studies on ionic liquids spread over solid surfaces (which can be taken as infinite radius solutes) have also revealed important aspects about the structure of these liquids [11,17–19]. These studies have shown a profile for the ion density oscillating from the surface, similar to the profile of the solvation layers of conventional molecular liquids [11,17–19]. It was also observed that the oscillation period is consistent with the dimensions of the component ions of the liquid. Moreover, it was demonstrated that extent of these oscillations from the surface depends inherently on the structure of the liquid [20]. In this Letter we studied the solvation of a molecular system of intermediate size: not so small that could be involved by electrostatic and van der Waals interactions domains of the ionic liquids and not large enough to cause the solvation layering. For this reason, we chose the molecule of fullerene C_{60} that has convinient size for analyzing the solvation of a practically uncharged nonpolar system. Such a system can cause the disruption of many intermolecular interactions in the solvent structure without forming new ones with the fullerene surface. Studies on the solvation of pure fullerenes in different solvents have been a subject of great importance for understanding the interactions between these carbonaceous nanostructures and other molecules [21,22].

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http://dx.doi.org/10.1016/j.cplett.2013.03.015

2. Simulations details

We employed extensive molecular dynamics (MD) simulations to investigate the structural and energetics aspects involved in the solvation of a hydrophobic and nonpolar nanosolute in ionic liquids. We examine these aspects in two ionic liquids: namely Ethylammonium Nitrate (EAN) and 1-Butyl-3-Methylimidazolium Tetrafluoroborate (BMIMBF4). These liquids were chosen because they are liquids at room temperature and also because they are in different positions at the E_T^N polarity scale [8] (see Figure 1); 0.676 to BMIMBF4 and 0.964 to EAN. Atomistic MD simulations using the isobaric-isothermal (NPT) ensemble were performed at 300 K under atmospheric pressure on a solution of one molecule of C_{60} fullerene in 600 ion pairs of $[EA]^+/[NO_3]^-$ and $[BMIM]^+/[BF_4]^-$ in cubic boxes with periodic boundary conditions employing the minimum image convention [23] (see Figure S1). Pure liquid have also been simulated and the results were used as our reference. The $[EA]^+$ and $[NO_3]^-$ ions were modeled using the parameters proposed by Hayes et al. [24]. For the BMIMBF4 the model developed by Liu and colleagues [25] and refined by Chaban and co-workers [14] was employed. The set of parameters for each liquid (and further details) is provided at Table S1 in the Supporting information.

For the ionic liquid–C_{60} interactions we chose a potential [26]. This potential model for the C_{60} is rather simple and does not take into account possible changes in the interaction energy due to the rearrangement of the electron density in fullerene cage caused by the environment. To quantify these effects due to the uncharged model for the C_{60} molecule, quantum calculations that explore the charge transfer between solute–solvent would be needed. We also observed that this model was developed to describe hydration properties, independently of the ionic liquids models. However, recently it has been shown that this same model is also adequate for describing the energetic properties of C_{60} in organic solvents [22]. Thus, we also expect the solvation of C_{60} in ionic liquids to be well described by this model.

To increase the efficiency and quality of the sampling, an equilibration procedure involving simulated annealing was performed, where the system was linearly heated from 300 to 900 K in 1 ns and thereafter cooled from 900 to 300 K in 1 ns. The system was kept at 300 K during additional 4 ns. Finally, for the production stage we have simulated 20 ns. Properties have been calculated considering a time-step of 2 fs with data collected every 0.05 ps. The systems were kept at the appropriate temperature and pressure via velocity rescaling [27] and Parrinello-Rahman [27] schemes, with constant couplings of 0.1 and 1.0, respectively. All bond lengths are constrained via the LINCS algorithm [28]. A cutoff of 1.2 nm to LJ interaction was used, while the Coulomb interactions were treated by using the PME algorithm [29]. MD simulations have been carried out using the Gromacs 4.5 program [30].

In order to estimate the solvation free-energy of the fullerene in both liquids, we propose the use of MD simulations combined with the thermodynamic integration algorithm [23] to obtain the transfer free energy of the fullerene between these liquids. In this

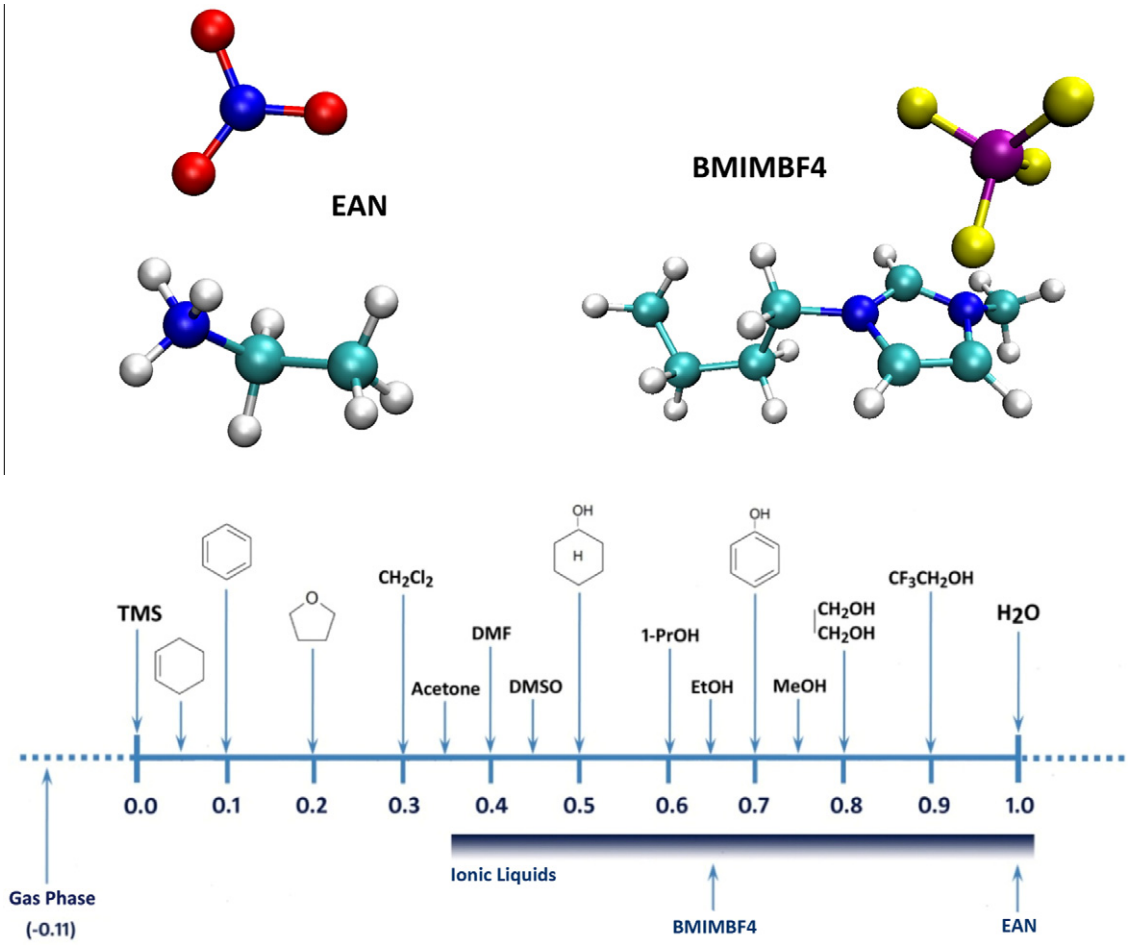

Figure 1. Above, component ion pairs of the studied liquids: Ethylammonium Nitrate (EAN) and 1-Butyl-3-Methylimidazolium Tetrafluoroborate (BMIMBF4). Below, normalized solvent polarity scale E_T^N (see Ref. [8]), where 0.0 corresponds to the polarity of the tetramethylsilane (TMS) and 1.00 to the water. EAN is more polar than water whereas BMIMBF4 has polarity comparable to that of phenol. Adapted from reference [8].

technique, free energies of transfer have been computed by decoupling a solute molecule from the solvent using the identity:

$$\Delta G = \int_{\lambda=0}^{\lambda=1} \left\langle \frac{dH(\lambda)}{d\lambda} \right\rangle d\lambda$$

where H is the parameterized Hamiltonian. The coupled state ($\lambda = 1$) corresponds to a simulation with the solute fully interacting with the solvent and the uncoupled state ($\lambda = 0$) corresponds to a simulation considering the solute in the absence of interactions with the solvent [23].

To avoid singularities, we have used the same soft-core potential for the LJ interactions: [31]

$$V_{SC}(r) = (1-\lambda)V([\alpha\sigma^6\lambda^p + r^6]^{1/6})$$

where $V_{SC}(r)$ is the normal hard-core pair potential, σ is the LJ size parameter of the pair of atoms, and $\lambda = 0$ and $\lambda = 1$ correspond to the fully coupled and uncoupled states, respectively. The parameters for the soft-core were $\alpha = 0.5$, $p = 1.0$, and $\sigma = 0.5$. This parameters set produces a smoother $dG/d\lambda$ curve for LJ interactions as it has been noticed by Shirts et al. [32]. For the Langevin thermostat we have used a friction coefficient of 1 ps^{-1}.

35 simulations of 15 ns were performed for each potential model and for each solvent, varying the value of the coupling parameter, λ, from 0 to 1. The increment of the coupling parameter ($\Delta\lambda$) varies according to the profile curve of the $dG/d\lambda$ depending on the smoothness of the graph. For the simulations in both EAN and BMIMBF4, we have used three different intervals for the $\Delta\lambda$ values.

3. Results and discussions

3.1. Structure

Firstly, we have calculated and compared the structure of ionic liquids around the fullerene C_{60}. The solvation structure of C_{60} was investigated on the basis of the center of mass radial distribution function (RDFs) $C_{60}\cdots$anion e $C_{60}\cdots$cation, as shown in Figure 2.

A general feature to be observed is the high structuring of the ionic liquids around the C_{60}. For both components of the ionic liquids, the RDF peaks were higher than the correspondent peaks for any RDFs of the pure liquids. For the $[BMIM]^+$ cation, e.g., we could observe a high and narrow peak near the C_{60} surface, which is a densification up to 2 times greater than that observed for the pure liquids. This densification is related to the size of the solute and is long-range effective, which could be evidenced by density fluctuations that persisted beyond 1.8 nm, mainly for EAN liquid. In fact, this effect, which does not occur in pure liquids, is mainly due to the strong van der Waals interactions between the nonpolar nanosolute and the aliphatic groups of the cations, leading to the structuring of these cations and consequently to the structuring of the anions as well. Additionaly, it is interesting to note that this structuring was qualitatively similar to that observed on solid surfaces where a regular oscillatory pattern with defined period was formed [17,20,33].

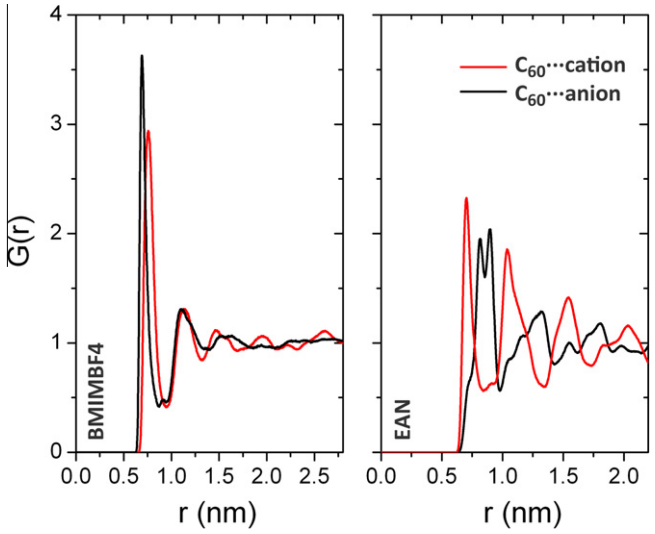

Figure 2. In black, radial distribution function (RDF) between the center of mass of the C_{60} and the center of mass of BMIMBF4 and EAN liquids. In red, RDF between center of mass of the C_{60} and center of mass of the imidazole ring, in the case of $[BMIM]^+$ cation, and between center of mass of the C_{60} and N atom in the case of the $[EA]^+$ cation.

The electrostatic charges in the ionic liquid were in relative motion which makes elusive the concept of solvation shell [1,8,10]. In order to quantify the number of molecules in the first layer? around the C_{60} in ionic liquids, we considered this first layer as the first solvation shell composed of anions and cations. This consideration can be justified by the RDFs which indicated a quasi-superposition of the first layers of cations and anions around the C_{60}. In the case of EAN there were, on average, 10 ionic pairs at the first solvation shell whereas in the solvation shell of the BMIMBF4 cation there were 9 ionic pairs. Figure 3 shows a representative configuration of the first solvation shell of both solutions.

We have observed that the interaction between the C_{60} and the nonpolar groups of the cations was quite pronounced and were differently structured in the first solvation shell. In the case of the $[BMIM]^+$ cation, the organization of its first shell was similar to that of the aliphatic tail, as well as to the imidazole ring, interacting alongside with C_{60} and covering the greater portion of its surface. In the case of $[EA]^+$ cation, on the other hand, the methyl groups tend to point toward the center of C_{60}, reducing the steric repulsion and allowing a higher number of molecules to assemble in the first shell. This behavior could be observed through the orientation distribution profile of the cations as a function of radial position from C_{60} center, presented at Figure 3. The $\cos(\theta)$ is defined as the angle between the radial vector and the vector perpendicular to the imidazolium ring for $[BMIM]^+$ or to the C–C–N plane for $[EA]^+$.

The three-dimensional solvation structure could/can? be better visualized by the spatial distribution function of the ions around the C_{60}. Figure 4 presents the isosurfaces for the cations and anions. We could clearly observe the difference in the spatial distribution of ions in each solution. For both cases the presence of cations near the surface of C_{60} was quite pronounced, but its relative spatial distribution showed distinct patterns. For both ionic liquids we could observe paired islands of cations whereas anions were evenly distributed around the surface of the solute. However, localization of anions was different in each solvent. In EAN liquid the anion islands were closer to the C_{60} surface, inside a spherical shell formed by cation density. Conversely, in BMIMBF4 the anions were assembled outside the cation density spherical shell, suggesting that the fullerene can partition preferentially into aliphatic domain. Notably, this result is in accordance with the solvation previously reported for smaller neutral systems [12]. Some aspects of this structural difference can be explained by the of solute–solvent interactions, particularly, in this case, by the interaction between the fullerene C_{60} and the cations of the ionic liquids.

3.2. Potential energy analysis

Table 1 presents the energy of the interaction between the fullerene C_{60} and the components of ionic liquids. As mentioned before, this interaction energy is composed of only the van der Waals interactions, U_{LJ}, since the potential model for C_{60} is

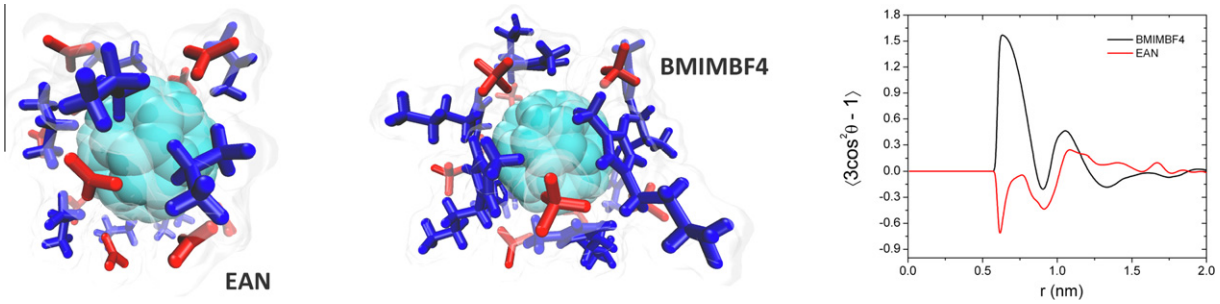

Figure 3. Representative simulation snapshots of the first solvation shell of the C_{60} in EAN and BMIMBF4. At right, the orientation distribution profile for the cations.

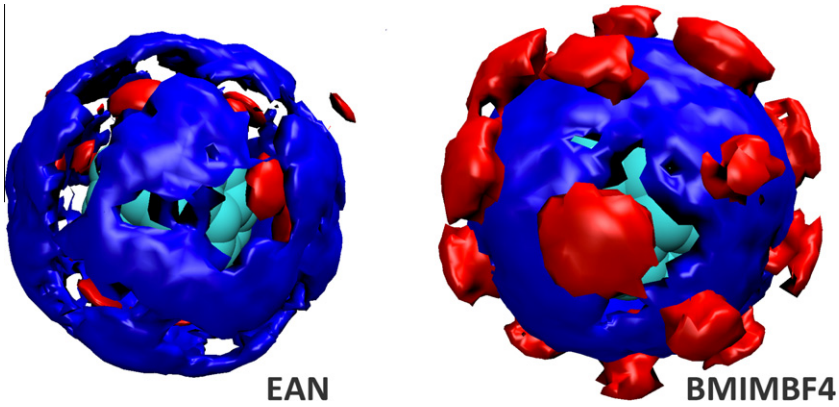

Figure 4. Spatial distribution functions of the ions centers around C_{60}: cations in blue and anions in red. At left we have the EAN and at right BMIMBF4 ionic liquids. Isosurfaces has been drawn at ~15 times average bulk density for anions and ~16 for $[EA]^+$ and $[BMIM]^+$ cations.

Table 1
Interaction energies between C_{60} and the components of the ionic liquids, U_{LJ}, (in kJ mol^{-1}). Uncertainty is less than 1%.

	C_{60} in EAN	C_{60} in BMIMBF4
U_{LJ} ($C_{60}\cdots$anion)	−137	−49
U_{LJ} ($C_{60}\cdots$cation)	−192	−205

uncharged. The values presented below, correspond to the number of ionic pairs in the system so that comparisons made with different systems should take this into account. We could observe that the total interaction energy was similar for both ionic liquids, −329 kJ mol^{-1} for EAN and −254 kJ mol^{-1} for BMIMBF4. However the energy for the separate components was quite different. The interaction energy of the fullerene with anions indicated a greater affinity with $[NO_3]^-$ (−137 kJ mol^{-1}) compared to the affinity with $[BF_4]^-$ (−49 kJ mol^{-1}). The higher affinity seems to affects the organization of the first solvation shell, explaining why $[NO_3]^-$ anions were, on average, slightly closer to C_{60} than $[BF_4]^-$, as observed by the RDFs. According to the expected, the interaction of C_{60} wit$[BMIM]^+$ was much larger than the interaction with $[EA]^+$ due to the alkyl groups of $[BMIM^+]$. In general, we see that the interplay of structural and energetic features of this interaction is the main responsible for the solvation properties of the C_{60} in these ionic liquids.

The energetic balance of the solvation of a nanoparticle, such as C_{60}, in ionic liquids is difficult to be quantified. Firstly, because solutions of nanometric size are usually larger than both polar and nonpolar domains, which causes the rupture of a large and strong network of interactions present in these domains leading to a serious enthalpic and entropic impact. Furthermore, the nature of the pure ionic liquids itself, with its highly charged components, large number of degrees of freedom and very slow dynamics, makes them a highly complex system ifself [1,7,11]. Nevertheless we can extract important information about the energetics of the system simply by analyzing the interaction energy between the components of the liquid and the solute (see Supporting information for further details in the case of the pure liquids).

At this point, a brief analysis of the energetics of the pure liquids regarding their polarities may be helpful. Coulomb (U_{Coul}) and van der Waals (U_{LJ}) components of the interaction energy between the constituents of the ionic liquids are shown in Table 2. Initially we could verify the greater polarity of the EAN liquid, comparing its component Coulomb with that corresponding to the BMIMBF4 liquid. We note, for example, that the interaction between the $[EA]^+$ and $[NO_3]^-$ ions was about 3.4 times stronger than the interacton between the $[BMIM]^+$ and $[BF_4]^-$ ions. Other indicative of the polarity of the EAN liquid is its smaller van der Waals energy compared to that of the BMIMBF4 liquid. In short, whereas the energetics of the EAN liquid was largely dominated by the electrostatic component, the energetics of the BMIMBF4 liquid presented a balance between both types of interactions.

Table 2
Coulomb (U_{Coul}) and van der Waals (U_{LJ}) components of the interaction energy between the constituents of the ionic liquids (in kJ mol^{-1}). Energy differences (ΔU_{Coul} and ΔU_{LJ}) between systems with and without fullerene. The differences were as calculated as $\Delta U = U_{solution} - U_{pure\ liq}$. Results for pure liquids are presented at Supporting information. Uncertaints is less than 1%.

	U_{Coul}	U_{LJ}	ΔU_{Coul}	ΔU_{LJ}
$[EA]^+$ – $[EA]^+$	128388	−8216	−282	33
$[EA]^+$ – $[NO_3]^-$	−336477	−12414	574	−15
$[NO_3]^-$ – $[NO_3]^-$	90631	−6321	−328	50
$[BMIM]^+$ – $[BMIM]^+$	41895	−22567	−91	39
$[BMIM]^+$ – $[BF_4]^-$	−99072	−14534	221	83
$[BF_4]^-$ – $[BF_4]^-$	17683	−983	−20	−2

The impact of the presence of the C_{60} on the energetics of the ionic liquids could be estimated through the difference between the ion interactions in the solutions and pure liquids. Table 2 shows these energy differences, ΔU_{Coul} and ΔU_{LJ}. It was possible to note here that in general, the interaction between ions of same sign is favored by the presence of C_{60}. In this sense, the total difference ($\Delta U_{Coul} + \Delta U_{LJ}$) for all interactions were negative and dominated by the electrostatic term. The most prominent case occurred for the interaction between the $[NO_3]^-$ anions, which in comparison to the corresponding interaction in pure EAN liquid presented a decrease of -278 kJ mol^{-1} ($-328 + 50$). In the case of EAN liquid, the total differences $\Delta U_{Coul} + \Delta U_{LJ}$ in cation–cation or anion–anion interactions were enough to counterbalance the effect of C_{60} in the cation-anion interactions which were strongly unfavored, especially in EAN where total difference was of 574 kJ mol^{-1}. For BMIMBF4 there was no effective balance, since the interaction cation-anion was destabilized by 221 kJ mol^{-1}. Overall, we have verified that the rupture of the ionic liquid network due to the presence of C_{60} destabilizes both liquids: EAN by 32 kJ mol^{-1} and BMIMBF4 by 230 kJ mol^{-1}. Here it is worthy to note that this is a pure energy analysis and that it should be regarded only as a sketch of the interactions between components of the solutions. A more rigorous analysis requires investigation of all aspects of the thermodynamics solvation, including the calculation of the solvation free energy.

3.3. Transfer free energy analysis

Solvation free energy is a statistical-mechanical quantity and its determination is not trivial even for simple systems. In the case of ionic liquids the problem is worsened since the determination is hampered by the presence of charges and many degrees of freedom. Besides that, ionic liquids present a very slow intramolecular dynamics. Conventional methods in many cases are not suitable for performing free energy calculations for ionic liquids. Previous studies on solvation in ionic liquids had used thermodynamic integration aiming the quantification of the chemical potential in excess of water and various small organic compounds in [C1mim][Cl] [34].

In the present Letter, we were interested in investigating the solvation free energy of the fullerene C_{60} in EAN and BMIMBF4 ionic liquids using thermodynamics integration. Our results indicated that C_{60} present a solvophobic character in both investigated ionic liquids. Furthermore, it was observed that this effect was much more pronounced in for the EAN liquid (more polar; $\Delta G = 323$ kJ mol^{-1}) than in the BMIMBF4 liquid (less polar, $\Delta G = 88$ kJ mol^{-1}). Relative free energy tends to reduce errors involved into the methodology and to introduce the concept of the free energy involved in the transfering C_{60} from one liquid to another. Our results indicated that, at room temperatures, the transfer of a single fullerene molecule from BMIMBF4 to EAN involves an increase of 235 kJ mol^{-1} in the free energy of the process. This increase in the free energy is around 2 times higher than that required to transfer C_{60} from water (as polar as EAN) to 1-butanol [35] (as polar as BMIMBF4) evidencing how the polarity of an ionic liquid can affect its solvation properties.

4. Summary and conclusions

In summary, we have carefully analyzed structural and energetic aspects of the solvation of fullerene C_{60} in two ionic liquids of different polarities at room temperature. We have found a highly structured layer of ionic liquid close to the surface of the C_{60} that extended over long distances (>1.8 nm) mainly in EAN liquid. The analysis of the spatial distribution of the ionic liquid revealed different patterns for the solvation of the C_{60} in both liquids. For both cases the presence of cations near the surface of C_{60} is quite pronounced, but their relative spatial distribution showed distinct patterns. For both ionic liquids we could observe paired islands of cations whereas anions were distributed evenly around the surface of the solute. This analysis suggests that the fullerene can partition preferentially into aliphatic domain. We also have noticed that compared to the interactions present in pure liquids, the presence of C_{60} weakened the ionic interactions present in the solution. This effect was more pronounced in BMIM ionic liquid, the less polar of the two liquids. Finally, based on our free energy calculations, we have showed that there is a energetic cost of 235 kJ mol^{-1} for transferring the fullerene C_{60} from BMIMBF4 to EAN. We believe that the current results will provide useful insights for understanding the solvation process of a hydrophobic solute as well as for understanding the experimental results involving fullerene at room temperature ionic liquids.

Acknowledgments

This Letter has been partially supported by the Brazilian agencies FAPESP and CNPq. The authors thank Dr. Dayane Tada for her critical review and comments.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2013.03.015.

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